



# PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

### Fungicidal Carbamic Acid Salts

We, FARBENFABRIKEN BAYER AKTIEN-GESELLSCHAFT, a body corporate organised under the laws of Germany, of 22c Leverkusen-Bayerwerk, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention is concerned with new fungicidal carbamic acid salts and with fungicidal compositions containing them. From US Patent Specification No. 2,317,765 alkylene-bis-dithiocarbamic acid salts are known which are distinguished by a good fungicidal activity. In this Specification there is described, *inter alia*, the preparation of an active compound of the aforesaid type by starting from propylene diamine, sodium hydroxide solution and carbon disulphide.

In a paper by Raymond W. Barratt and James G. Horsfall, Connecticut Agricultural Experiment Station, New Haven, Bulletin 508, June 1947 entitled "Fungicidal Action of Metallic Alkyl Bisdithiocarbamates", there is further described (page 7) the disodium salt of isopropylene-bis-dithiocarbamic acid, and the Table on page 9 of this paper shows that the activity of the sodium salt of ethylene-bis-dithiocarbamic acid is a multiple of that of the sodium salt of iso-propylene-bis-dithiocarbamic acid.

We have now found that the manganese salt of iso - propylene - bis - dithiocarbamic acid is distinguished by an especially good activity, particularly in comparison with the compounds described in the above-mentioned US Patent Specification. The activity of this isopropylene compound is greater by a multiple than that of all the normal propylene compounds mentioned in the patent specification.

The finding that the manganese salt of isopropylene-bis-dithiocarbamic acid possesses these extraordinary properties is especially surprising, since it is known from the above-

mentioned paper by Barratt and Horsfall that sodium salts show the contrary.

The compound according to the present invention can be prepared, for example, by reacting 1,2-propylene-diamine with carbon disulphide, preferably in the presence of an alkali metal hydroxide or ammonium hydroxide, and further reaction with salts of manganese.

The compound according to the present invention is active chiefly against fungal pests against which conventional dithiocarbamic acid salts have previously been employed, i.e. especially against *Phytophthora infestans*, *Cladosporium fulvum* or *Alternaria solani* on tomato and potato plants, against *Peronospora* (= *Plasmopara viticola*) on grape vines, *Venturia inaequalis* on fruits with pips, and against similar fungal pathogens of other plants.

The compound according to the present invention is applied in known manner, i.e. preferably in combination with suitable solid or liquid extenders or diluents, optionally in the presence of suitable emulsifiers or wetting agents. The compound is preferably used in aqueous dilution, together with non-ionic emulsifiers and/or wetting agents, and, if desired, an inert solid formulation assistant. It may also be used with other fungicides and/or insecticides.

The production of the compound according to the invention may be briefly described as follows:—

0.255 kg. 1,2-propylene-diamine are dissolved in 1.87 litres water. To this solution there are added dropwise 0.55 kg. carbon disulphide. 0.555 kg. of a 46% sodium hydroxide solution are then added.

The solution (0.833 kg. 100%) is further reacted with a manganese salt solution (manganese sulphate). Yield 0.426 kg. methyl-ethylene-bis-(dithiocarbamic acid) manganese salt with 51.7% content (after splitting off carbon disulphide).

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According to a preferred method of production, the compound according to the present invention may also be produced directly from propylene dichloride, as can be seen from the following brief instruction.

37.7 g. propylene dichloride and 396.0 g. of a 35.8% ammonium hydroxide solution are reacted at 78—80° C. for 32 hours in an autoclave provided with stirrer, until the propylene chloride disappears. The solution is concentrated to dryness *in vacuo* and the residue taken up in 210 ml. water.

To this aqueous solution there are added 80 g. of a 46% sodium hydroxide solution and 54 g. carbon disulphide at 38—40° C. (while maintaining a pH value of below 10) within about 8 hours. After the addition of a little kieselguhr, the solution is filtered off with suction. This solution is treated with an aqueous solution of manganese sulphate and the precipitated manganese salt filtered off with suction and dried. Yield: 48 g. of 85% (after splitting off carbon disulphide) of methyl - ethylene - bis - (dithiocarbamic acid) manganese salt.

Instead of the pure propylene chloride, a propylene chloride-containing petro-chemical by-product may be employed.

The following Example is given for the purpose of illustrating the properties of the compound according to the present invention:—

#### EXAMPLE

Young tomato plants (Bonny Best) are sprayed drip-wet with aqueous suspensions containing the active material in the concentrations given below. After 24 hours, the tomato plants are inoculated with a spore suspension of *Phytophthora infestans*. The plants are then placed in a humidity chamber with 100% atmospheric humidity and at a temperature of 20° C. After a period of 5 days, the degree of attack is determined as a percentage based on the untreated but inoculated control plants. The degree of attack on the untreated control plants is taken as 100. The results obtained are given in the following Table:

TABLE

*Phytophthora infestans* on tomatoes

Active material	Concentration of active material in aqueous suspension in %	Degree of attack in % of the untreated control (=100): average value from 5 tests
1 Manganese-isopropylene-bis-dithiocarbamate (according to the invention)	0.025	5
zinc-isopropylene-bis-dithiocarbamate	0.025	12
2 manganese-isopropylene-bis-dithiocarbamate (according to the invention)	0.0062	16
manganese-ethylene-bis-dithiocarbamate	0.0062	21

As can be seen from the above Table, the fungicidal action of manganese-isopropylene-bis-dithiocarbamate is superior not only to that of zinc - isopropylene - bis - dithiocarbamate but also to that of manganese-ethylene-bis-dithiocarbamate: the plants treated with the fungicide according to the present invention show the smallest degree of attack by *Phytophthora infestans*.

WHAT WE CLAIM IS:—

1. The manganese salt of isopropylene-bis-dithiocarbamic acid.

2. Fungicidal compositions containing the manganese salt of isopropylene-bis-dithiocarbamic acid and a solid or liquid extender or diluent.

3. Fungicidal compositions according to claim 2, wherein there is additionally present an emulsifier and/or wetting agent.

4. Fungicidal compositions according to claim 2 or 3, wherein the liquid extender or diluent is water, together with a non-ionic emulsifier and/or wetting agent.

5. Fungicidal compositions according to claim 2, substantially as hereinbefore described and exemplified.

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